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INTEROFFICE CORRESPONDENCE
Richmond, Virginia

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From: J. M. Garman / C. H. Callicutt *JMG CHC*

Subject: Massachusetts Compliance: Determination of pH of an Aqueous Solution of Mainstream Smoke

The Product Testing Laboratory (PTL) was charged with determining the pH of mainstream smoke in an aqueous solution in compliance with the Massachusetts Regulations dated August 19, 1997. This memo contains PTL's results in preparation for the implementation of this analysis. Included are a comparison of pH results for 44 mm Cambridge filter pads from different manufacturers, pH results obtained for the Whatman Cambridge filter pad, pH results for the degassed water, pH results obtained for IM#15, a pH reproducibility study using IM#16, and results obtained for Kentucky Reference cigarettes. The apparatus and methodology was developed based on Philip Morris's Product Research Division (PRD) Method Number M-2-A, "Analysis of Mainstream Smoke for pH and Reduction-Oxidation Potential (Redox) in an Aqueous Solution," September 11, 1997, and Battelle Northwest Standard Operating Procedure AC-3A3P-00, "Analysis of pH and Redox Potential in Mainstream Smoke Collected in an Aqueous Solution, June 24, 1997. An initial PTL procedure which is attached was prepared prior to the initiation of pH testing. Modifications were made in the development of PTL's testing methodology, as noted within this memo, and the apparatus and methodology used for determining the pH of Massachusetts Compliance samples is documented in the attached PTL procedure written in ISO format.

Initially, pH analyses were performed on the same day on each type of 44 mm Cambridge filter pad available within PTL. Below are the determined pH measurements utilizing one pad in 100 mL of degassed water after magnetically stirred for 5 minutes:

TABLE I: pH Comparison of Cambridge Filter Pads

	Whatman	Gelman	Performance Systematix
Replicate 1	8.324	8.148	7.734
Replicate 2	8.267	8.184	7.264
Replicate 3	8.600	8.207	7.473
Replicate 4	8.127	8.290	7.300
Average	8.330	8.207	7.443
Standard Deviation	0.20	0.06	0.21

The Whatman filter pads were utilized for all subsequent pH determinations as they are the only commercially available filter pads certified to meet ISO 3308 specifications. Utilizing the same pH procedure to generate the filter pad comparison data, the following pH results were obtained for the Whatman pads during the period of 10/6/97 to 10/17/97:

Table II: pH Results for Whatman Cambridge Filter Pads

Date of Analysis	pH Result
10/6/97	8.324
10/6/97	8.267
10/6/97	8.600
10/6/97	8.127
10/8/97	8.306

Date of Analysis	pH Result
10/9/97	8.289
10/10/97	7.962
10/15/97	7.695
10/16/97	8.046
10/17/97	8.119
Overall Average	8.174
Standard Deviation	0.24
Determinations	10

All water utilized in this study was degassed as specified in the attached PTL final procedure. The pH results obtained for the different bottles of degassed, HPLC grade water are listed below:

Table III: pH Results for Degassed Water

Bottle Number	Date Degassed	Date of Analysis	pH Result
1	10/5/97	10/6/97	6.054
1*	10/5/97	10/8/97	6.052*
2	10/7/97	10/8/97	6.647
3	10/15/97	10/17/97	5.925
4	10/16/97	10/17/97	6.254
Average			6.220
Standard Deviation			0.32

* pH result not included in average

The bottles of degassed water exhibited a larger variation than the filter pad-containing degassed water. The pH of the sealed Bottle #1 was repeated two days later showing that the pH failed to change. The bottle to bottle variation was theorized to be the result of the extremely low ionic concentration of this water.

The PRD and Battelle procedures include a smoking blank. Only one result was obtained using FTC smoking parameters and three results were obtained using Massachusetts protocol parameters prior to commencing with actual sample testing. All results were obtained by drawing 10 puffs through one unlit IM#16 monitor cigarette allowing each puff to bubble through the water-containing impinger tubes. The cigarette was removed from the apparatus and two clearing puffs were drawn through the water-containing

impinger tubes. The impinger solutions were combined in a beaker and the TPM pad was added.

Table IV: pH of the Smoking Blank

Date of Analysis	pH Result
10/6/97 (FTC)	7.062
10/15/97 (MA)	6.977
10/16/97 (MA)	6.969
10/17/97 (MA)	7.053

Following are the results for the pH determination for Industry Monitor (IM) #15 following FTC protocol, (equilibration and puff parameters), using one cigarette per determination:

Table V: FTC pH Results for IM#15

Date of Analysis	pH Result
10/6/97	5.192
10/6/97	5.141
10/6/97	5.172
10/6/97	5.178
Average	5.171
Standard Deviation	0.022

Although PTL routinely utilized IM#16 at the time of this study, IM#15 data was obtained in order to compare results obtained for the Philip Morris Method M-2-A. The IM#15 results per that procedure were pH = 5.45, (Standard Deviation = 0.11 : N = 40).

A reproducibility study was conducted in which ten determinations on IM#16 were performed on each of three consecutive days. Within each subgroup of ten, the cigarette holder impinger orifice tube was rinsed with aliquots of the resultant aqueous solution after smoking for five of the replicates while no rinsing was performed on the other five replicates. This variation in procedure was performed to ascertain if this rinsing step was significant. The smoking was performed following the Massachusetts protocol using one cigarette per replicate.

The statistical evaluation of the results was performed per the attached memo, C. Boswell to J. Garman, "pH on Aqueous Solution Analysis," October 16, 1997. The results, shown in Table VI did show a slight, (0.020), but statistically significant, pH difference between orifice tube rinsed results and non-rinsed results. Even though the obtained difference was very small, orifice tube rinsing was performed on all subsequent analyses.

Utilizing the same data, the obtained confidence interval for ten replicates was found to be ± 0.019 while five replicates produced a ± 0.027 confidence interval. It was decided that five replicates per sample would be utilized for routine sample testing.

Table VI: Results of IM#16 pH Reproducibility Study

Rinsing of Impinger Tube	pH Result	No Rinsing of Impinger Tubes	pH Result
10/8/97	5.351	10/8/97	5.350
Standard Dev.	0.016	Standard Dev.	0.019
Replicates	5	Replicates	5
10/9/97	5.3248	10/9/97	5.327
Standard Dev.	0.033	Standard Dev.	0.021
Replicates	5	Replicates	5
10/10/97	5.350	10/10/97	5.344
Standard Dev.	0.027	Standard Dev.	0.036
Replicates	5	Replicates	5
Average	5.359	Average	5.340
Standard Deviation	0.021	Standard Deviation	0.027
Replicates	15	Replicates	15

Overall Average	5.350
Standard Deviation	0.025
Replicates	30

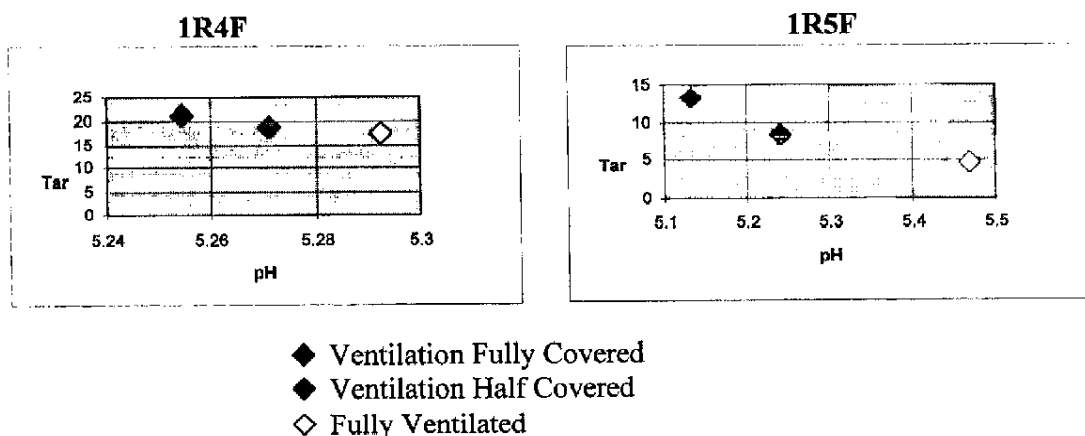
The 2R1F, 1R3F, 1R4F, and 1R5F Kentucky Reference Cigarettes were analyzed for pH per the Massachusetts smoking protocol utilizing one cigarette per each of five replicate determinations. All four versions were analyzed without applying tape over the tipping paper. The 1R4F and 1R5F versions were also analyzed with the tipping paper half taped and fully taped. The results are listed below:

Table VII: pH results for Kentucky Reference Cigarettes

Sample	pH (As Is)	pH (Half Taped)	pH (Fully Taped)
2R1F	5.281	-	-
Stand. Dev.	0.027		
Replicates	5		
1R3F	5.253	-	-
Stand. Dev.	0.028		
Replicates	5		
1R4F	5.292	5.270	5.252
Stand. Dev.	0.079	0.031	0.044
Replicates	5	5	5
1R5F	5.461	5.235	5.127
Stand. Dev.	0.052	0.039	0.040
Replicates	5	5	5

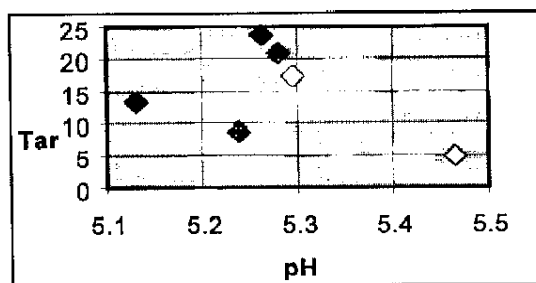
Following, is a graphical representation of what appears to be a correlation between the tar and pH for the 1R4F and 1R5F. As more ventilation is covered, the resultant pH result decreases as the tar result increases.

Figure I: Tar versus pH for 1R4F and 1R5F



This correlation is only valid for ventilation differences for a specific cigarette brand and not a global tar to pH correlation as graphically shown for the combined 1R4F and 1R5F data below:

Figure 2: Tar versus pH for 1R4F and 1R5F Combined

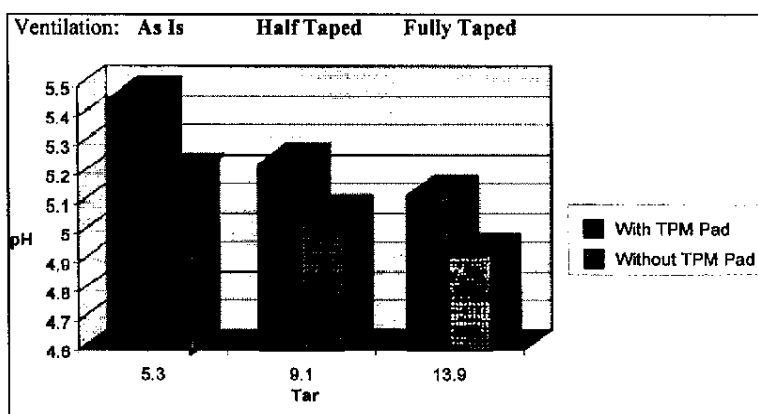


In order to investigate the effect of the TPM pad within the pH determination, the 1R5F sample was analyzed for pH following the same procedure with the exception of not including the TPM-containing filter pad into the resultant aqueous solution. The results listed in Table VII for 1R5F were used as the control. The comparison results are shown in Table VIII. The omission of the TPM-containing pad results in a decrease of 0.21 ± 0.04 pH units for the three levels of ventilation. The pH results with and without the TPM-containing filter pad are graphically shown in Figure 3.

Table VIII: pH Results for 1R5F With and Without TPM Pad

Sample	Date	pH (As Is)	pH (Half Taped)	pH (Fully Taped)
1R5F With TPM Pad	10/15-17	5.461	5.235	5.127
Stand. Dev.		0.052	0.039	0.040
Replicates		5	5	5
IM#16 With TPM Pad	10/15-17	5.339	N/A	N/A
Stand. Dev.		0.028	N/A	N/A
Replicates		6	N/A	N/A
1R5F W/O TPM Pad	10/22	5.201	5.059	4.929
Stand. Dev.		0.028	0.072	0.041
Replicates		4	4	4
IM#16 With TPM Pad	10/22	5.326	N/A	N/A
Stand. Dev.		0.036	N/A	N/A
Replicates		4	N/A	N/A
1R5F Difference Due to Pad		0.260	0.176	0.198

Figure 3: Effect of TPM-Containing Filter Pad on the pH of 1R5F



The number of cigarettes smoked per determination was evaluated. One, five, and ten 1R5F cigarettes were smoked through the apparatus per determination. The pH measurement was performed separately on the aqueous solution from the front and back impinger. The results are listed in Table IX.

Table IX: The Effect of the Number of Cigarettes per Determination of pH for 1R5F

Number of Cigarettes per Determination	pH of Front Impinger Aqueous Solution	pH of Rear Impinger Aqueous Solution
10	6.120	4.947
5	5.336	4.938
1	5.314	4.990

The results showed that the pH of the aqueous solution from the rear impinger was significantly more acidic than from the front impinger. The pH of the rear impinger aqueous solution for the three sampling sizes was consistent at 4.96 ± 0.02 . The front impinger aqueous solution was consistent for the one and five cigarette sample sizes at 5.33 while the pH for the ten cigarettes per determination was significantly higher at 6.12.

As the results showed no difference for one and five cigarettes per determination, it was decided to utilize two cigarettes per determination. It was also decided to decrease the number of sample replicates from five to three. Tables X, XI, and XII lists comparative pH results for IM#16, the IM#16 smoking blank, and Kentucky Reference Cigarettes, respectively, using one versus two cigarettes per determination.

Table X: pH of IM#16

	1 Cigt/Determination*	2 Cigt/Determination**
Average	5.359	5.348
Standard Deviation	0.021	0.032
Replicates	15	14

* From Table VI (Rinsed Impinger Tube results)

** Obtained over duration of Massachusetts Compliance sample testing

Table XI: pH of Smoking Blanks

	1 Cigt/Determination*	2 Cigt/Determination**
Average	7.000	7.112
Standard Deviation	0.046	0.122
Replicates	3	14

* From Table IV (Massachusetts Protocol)

** Obtained over duration of Massachusetts Compliance sample testing

Table XII: pH of Kentucky Reference Cigarettes

Sample	pH 1 cigt/Determination*	pH 2 cigt/Determination**
2R1F	5.281	5.309
Stand. Dev.	0.027	0.013
Replicates	5	3
1R3F	5.253	5.304
Stand. Dev.	0.028	0.016
Replicates	5	3
1R4F	5.270	5.354
Stand. Dev.	0.031	0.016
Replicates	5	3
1R5F	5.235	5.304
Stand. Dev.	0.039	0.016
Replicates	5	3

* Obtained from Table VII

** 1R4F and 1R5F tested on 11/13 and 2R1F and 1R3F on 11/20

During the period from 10/29/97 to 11/12/97, the twenty current packings of the Marlboro brand family were tested for pH as per the attached final PTL procedure.

Attachments

Distribution

L. Chambers
C. Connell
R. Cox
W. Dwyer
F. Hsu
K. Podraza
J. Whidby
PTL Files
Central Files